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KNUDSEN CELL STUDIES OF Ti-Al THERMODYNAMICS

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ABSTRACT

In this paper we describe the Knudsen cell technique for measurement of thermodynamic activities in alloys. Numerous experimental details must be adhered^{to} in order to obtain useful experimental data. These include introduction of an *in-situ* standard, precise temperature measurement, elimination of thermal gradients, and precise cell positioning. Our first design is discussed and some sample data on Ti-Al alloys is presented. The second modification and associated improvements are also discussed.



INTRODUCTION

The most common method for high temperature vapor pressure measurement is the Knudsen cell mass spectrometric (KCMS) technique (1). In this approach, a condensed phase is equilibrated with its vapor in a small enclosure. An orifice of well-defined geometry allows a small amount of the vapor to be sampled for analysis. The vapor must be of sufficiently low pressure so that molecular flow is attained. The vapor emerging from the orifice is ionized, sorted according to molecular weight, and a resultant ion current is measured. After careful calibration, the ion current from the mass spectrometer may be converted to reliable vapor pressures (2).

A large amount of excellent data has been obtained on pure materials from this technique over the past fifty years. Several groups are currently applying this technique to measure vapor pressures over alloys and thus obtain thermodynamic activities (3-7). In order to obtain such data, a number of critical experimental issues must be addressed. In this paper we discuss these issues and our approaches to solving them.

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EXPERIMENTAL

The critical component in these types of measurements is the Knudsen cell furnace and associated hardware. This is typically on a vacuum flange that mounts in a chamber with a high-capacity vacuum pump. The cell can be heated with either a resistance heater or an electron bombardment heater. A small portion of the effusate distribution is selected to form a well-defined molecular beam, which is directed into the ion source chamber. We use a magnetic sector mass spectrometer with an electron impact ionizer[#].

Typically a standard material with a known vapor pressure is examined with this system for calibration. Assuming the temperature has been calibrated, the calibration constant can be derived from the following equation (8):

$$P_i = \frac{kI_i T}{\sigma_i} \quad (1)$$

Here P_i is the pressure inside the cell, k is the calibration constant, I_i is the measured ion intensity, T is the temperature of the sample inside the cell and σ_i is the ionization cross section of the molecule being measured.

In a conventional single cell mass spectrometer, samples must be changed from the calibration standard to the alloy sample under study. Herein lies the major issue for thermodynamic activity measurements with mass spectrometry. In most mass spectrometers, when the vacuum is broken, the calibration constant changes. For this reason, it is desirable to have an *in-situ* standard. This is accomplished by use of a multiple Knudsen cell configuration. Several investigators have used such flanges (4-7). Our designs are illustrated in Figures 1 and 2.

There are several challenging experimental issues, which must be addressed in such a configuration (9):

1. Background subtraction.
2. Contamination of the molecular beams from the vapor inside the heat shields.
3. Identical sampling and ionization of molecular beams emerging from all cells.
4. Accurate temperature measurement.
5. Isothermal conditions within cells and between cells.

Background subtraction is an important issue with all mass spectrometers. Even a very clean vacuum will contain background gases, which may overlap the vapor from the Knudsen cell. The easiest way to solve this problem is with a simple shutter plate which interrupts the molecular beam. This shutter must be located in a position which does not also interrupt background gases from the Knudsen cell vacuum chamber itself.

[#] HT-90-12, Nuclide/Spectrumedix, State College, PA

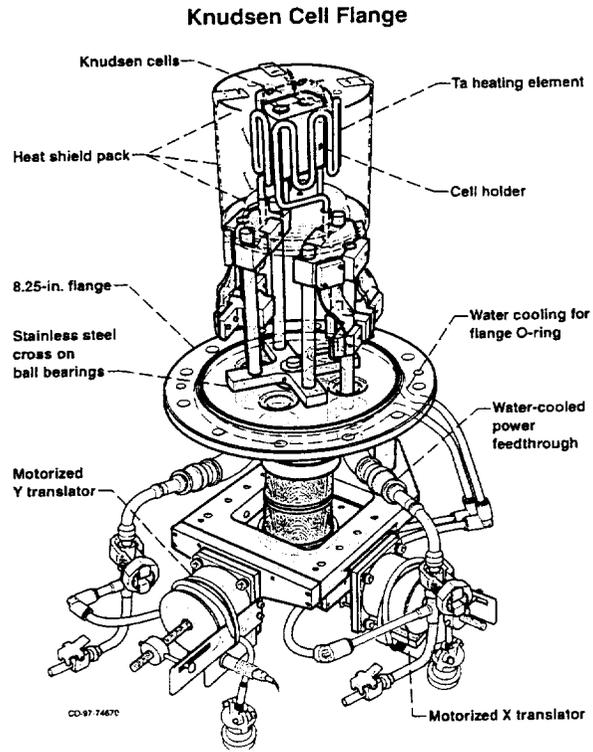


Figure 1. First design—double Knudsen cell flange.
Multiple Knudsen Cell Flange

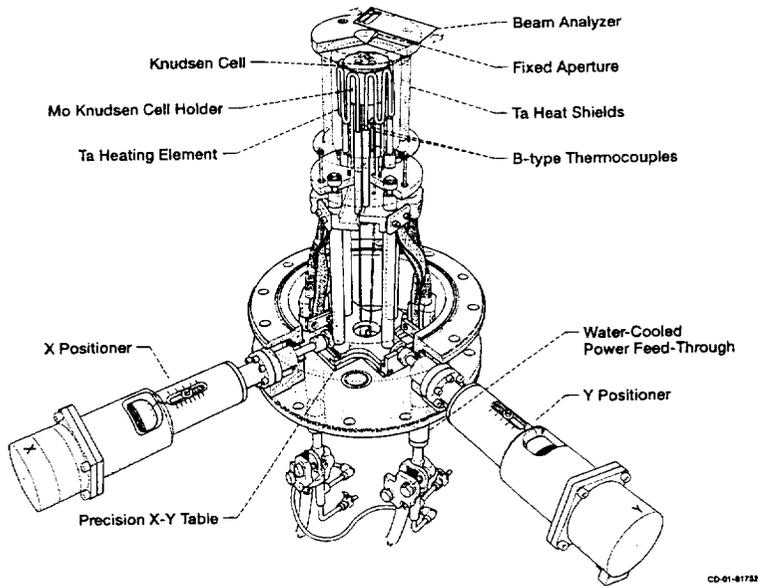


Figure 2. Second design—multiple Knudsen cell flange.

Consider next the problem of cross contamination. Suppose we are measuring the activity of Al in a TiAl alloy. An Al standard is in one cell and a TiAl alloy is in another cell. We want to measure the vapor pressure of Al and then the vapor pressure of Al in TiAl. The larger pressure and correspondingly more intense molecular beam from the pure Al containing cell must not add to the weaker molecular beam from the Ti-Al alloy.

Cross contamination occurs due^{to} a portion of the effusing vapor being trapped in the heat shield pack. The vapor emerging from a cell forms a distribution in accordance with the cosine law (2). Typically only a small solid angle close to the normal passes through the holes in the heat shields and is sampled by the mass spectrometer. The higher angle effusate is trapped inside the heat shield pack. This "heat shield vapor" condenses on the inner heat shield walls and heating element and then re-evaporates. This is typically not a problem for a conventional single Knudsen cell system. However, with multiple cells, the "heat shield vapor" emerges through the heat shield holes co-linear to the molecular beam. When the vapor pressure of a specie from an alloy is much lower than its pure reference state, the "heat shield vapor" can be a significant source of error. Thus in our Al/TiAl example, the molecular beam emerging from the TiAl cell may have an erroneously high Al intensity due to contamination.

There are several routes to solve this problem. Our approach is to use a different standard material, i.e. Au or Cu in place of Al. The necessary corrections are made for the different vapor pressure and cross section of the substitute standard in place of Al. We have further refined our heat shield and orifice design to put the cell orifices as close to the top of the heat shield pack as possible (Figure 2). This also puts the cell orifices closer to the ionizer, which improves sensitivity.

Related to this issue of sampling the *true* molecular beam from each cell is the third experimental consideration. In order compare vapor pressures, the interaction volume of the molecular beam and the ionizing electrons must be *exactly* the same for each cell. This is accomplished via precise movement of the cells and accurate definition of the molecular beam emerging from the cell orifices.

In our first design the cell and furnace was mounted on a commercial x-y positioner** outfitted with stepper motors. The cell was moved into position with a 'joystick' controller and observed visually with the telescope from the optical pyrometer.

In the second design, positioning was considerably refined. A more precise x-y positioner was designed and fabricated in-house. This system is operated by computer controlled stepper motors. The second design also includes additional apertures for better definition of the molecular beam. The copper plate separating the Knudsen cell chamber from the ionization chamber contains a small orifice in the center, as shown in Figure 2. A second aperture adjacent to the ionizing filament further defines the beam. The cell is precisely moved to line up with the apertures by monitoring ion intensity with position. Further confidence is gained by visual monitoring with a TV camera, mounted above the ionizer.

** MDC Vacuum Components, Hayward, CA

Accurate temperature measurement is another important issue in vapor pressure measurement. Since vapor pressure is exponentially dependent on temperature, small errors in temperature measurement may lead to large errors in calculated vapor pressures. Either thermocouples or optical pyrometry may be used to measure temperature. In either case it is critical that the measurement be taken on the cell or as close to the cell as possible. Our first measurements were done with a disappearing filament type pyrometer. We have found that thermocouples must be tightly coupled to the cell for more accurate temperature measurement. Also, thermocouples are more suitable for data acquisition. Temperatures are calibrated with known melting points of pure materials. On heating and cooling, a clear plateau is observed in vapor pressure.

Isothermal conditions within the Knudsen cell are a critical issue. In most configurations, the furnace is quite small and the cell is held in place on the bottom with support rods. The support rods are often a path for heat escape. Thus special design efforts must be made to minimize the thermal gradient. Thermocouples on the bottom and top of the cell provide a direct measure of the gradient. Our first design uses cells with a height to diameter ratio of two; the second design uses cells with a height to diameter ratio of one. The second cells have less possibility of a gradient and allow more accurate vapor pressure measurement due to reduced Clausing factor effects (2).

Our initial measurement procedure involved deriving a calibration constant from the standard. A series of data points were collected and a 'second law' heat derived:

$$\ln I_i T = A + \frac{B}{T} \quad (3)$$

The tabulated values for the standard were fitted to this same equation:

$$\ln P_i = C + \frac{D}{T} \quad (4)$$

Now the calibration constant was derived from putting equations (3) and (4) into equation (1):

$$\ln\left(\frac{k}{\sigma_i}\right) = \ln\left(\frac{P}{I_i T}\right) = \left(C + \frac{D}{T}\right) - \left(A + \frac{B}{T}\right) \quad (5)$$

This calibration constant was then used to determine the vapor pressures of a particular specie over the alloy (7).

The measurement procedure for the second design (Figure 2) is improved. We measure the effusing vapor from each cell at given temperature. The standard provides the calibration constant from equation (1). This is applied to directly calculate a vapor pressure above the alloy and hence the thermodynamic activity. Further, the second design contains three cells so that two standards can be used and two component activities can be measured. This 'single temperature' approach should make automation of the procedure easier.

RESULTS

To date, we have a number of results on Ti-Al and Ti-Al-Cr alloys taken with the first design (7). Figures 3(a) and (b) illustrate some results on Ti-45Al for both Al and Ti activities, respectively.

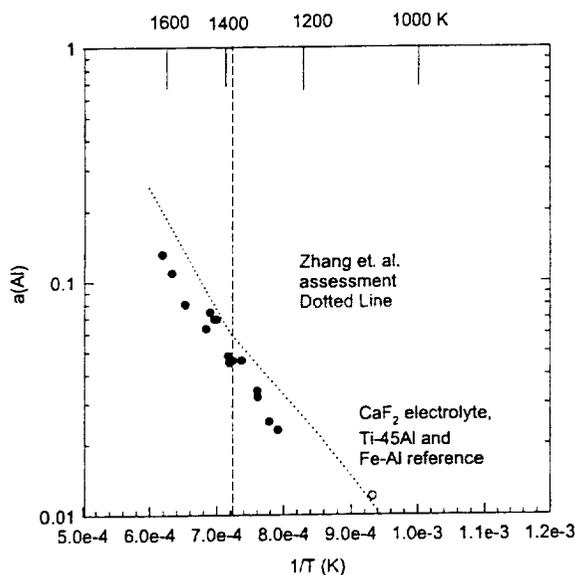


Figure 3(a). Measurements of Al activity in Ti-45 a/o Al.

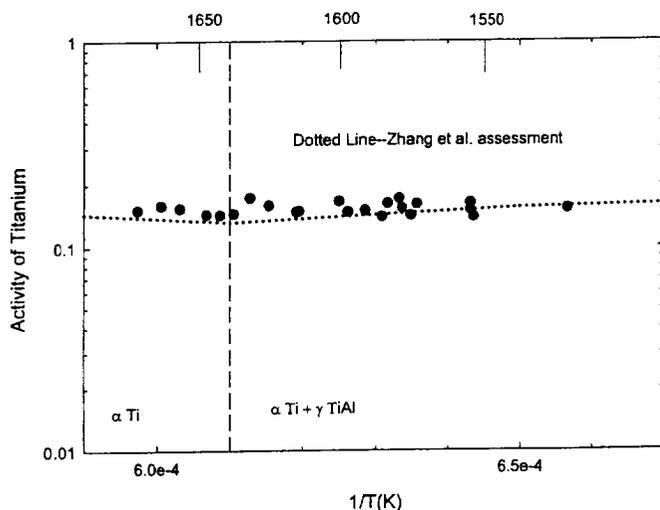
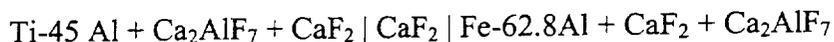


Figure 3(b). Activity of Ti in Ti-45Al compared to recent assessment.

Note that the data shows good agreement with a recent assessment of the Ti-Al system (11), which was done independently of these data. This indicates our data is consistent with other thermodynamic measurements and phase boundary measurements on this system. Also, as part of this study the activity of Al in Ti-45Al in the following electrochemical cell at 1073 K. The Knudsen cell data is reasonably consistent with this result, as shown in Figure 3(a).



Selected other binary Ti-Al alloys and ternary Ti-Al-Cr alloys have been studied with this method (7). In general, Cr additions near γ -TiAl have little effect on the activities of Ti or Al. Thus the improved oxidation behavior of Ti-Al-Cr alloys over Ti-Al alloys does not appear to be due to a thermodynamic effect.

Current work involves the addition of oxygen near the α_2 -Ti₃Al phase, which shows substantial oxygen solubility. Initial results suggest that the oxygen tends to decrease Ti activity and increase Al activity.

SUMMARY AND CONCLUSIONS

We have discussed our work in developing a multiple Knudsen cell instrument for precise measurements of activities in alloys. This is a challenging experimental technique and a number of considerations must be addressed. These include: background subtraction, accurate positioning of the cells, cross contamination of molecular beams from different cells, identical sampling and ionization of molecular beams from different cells, and isothermal conditions within cells and between cells. We discuss our approaches to each of these and our experimental apparatus for making these measurements. Examples from Ti-Al alloys illustrate the data.

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